

## Thermovoltaic Effect in Polycrystalline Samarium Sulfide

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Received May 26, 2009

**Abstract**—A thermovoltaic effect has been observed for the first time in a polycrystalline sample of samarium sulfide (SmS) with artificially created concentration gradient of excess (overstoichiometric) samarium ions, in which an electric voltage of 12–22.5 mV was generated in a temperature interval of 370–485 K. It is shown that the specific voltage generation in SmS due to the thermovoltaic effect can be observed in a temperature range of 100–1800 K.

PACS numbers: 72.15.Jf, 73.40.Sx, 68.35.Fx

DOI: 10.1134/S1063785009110030

It is known that uniform heating of samarium sulfide (SmS) samples in the absence of external temperature gradients leads to the appearance of electric voltage across the sample. A necessary condition for this phenomenon is the presence of a gradient of the concentration of defect (off-site) samarium ions in excess of their stoichiometric content in the crystal lattice [1]. Recently [2], this thermovoltaic effect has been observed in a bilayer thin-film SmS-based sandwich structure, where the necessary gradient of samarium concentration was created using controlled deviation from the stoichiometric composition.

This Letter presents the results of various experiments on the observation of a thermovoltaic effect in a volume polycrystalline SmS sample, in which the concentration gradient of excess (overstoichiometric) samarium ions was artificially created by means of thermodiffusion.

The sample in the form of a parallelepiped with dimensions  $4.4 \times 6.8 \times 7.7$  mm was prepared from polycrystalline SmS possessing the typical electrical properties, crystal lattice parameter, and X-ray coherent scattering domain (CSD) size ( $\sim 800$  Å). A solution of  $\text{SmCl}_3$  was applied onto one large face of the polycrystalline sample. Then, the sample was dried and annealed in argon for 3 h at  $T = 1100^\circ\text{C}$ . The duration and temperature of the annealing was selected so as to ensure a penetration depth of  $x \sim 0.5$  mm for diffusing excess samarium ions. This depth is determined as follows:

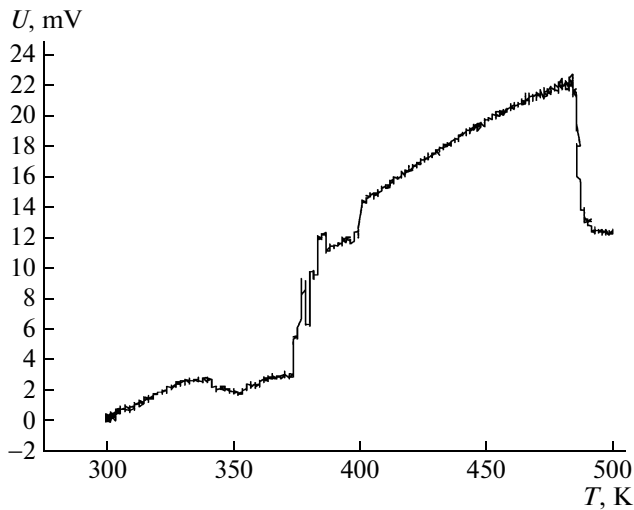
$$x = \sqrt{2Dt}, \quad (1)$$

where  $D$  is the diffusion coefficient of samarium ions in SmS. Unfortunately, the  $D$  value for this system is yet not measured. For this reason, the diffusant penetration depth was estimated using the known diffusion

coefficient of europium in SmS ( $D = 10^{-7}$  cm<sup>2</sup>/s [3]), since Eu is a closest analog for Sm. Indeed, Eu has a close atomic weight, electron structure, and approximately the same monosulfide crystal lattice parameter ( $a_{\text{EuS}} \approx a_{\text{SmS}} \approx 5.97$  Å). After the diffusion annealing, nickel contact pads were formed by thermal deposition on the opposite large faces (spaced by 4.4 mm) of the sample.

The experimental procedure was as follows. The sample was pressed with one metal-coated surface to a flat resistive heater. The output voltage (thermo emf) was measured between contact pads with clamped current leads. The sample temperature was monitored by two thermocouples with junctions attached to the contact pads. All this system was placed in a forevacuum chamber. The sample was smoothly heated at a constant electric power supplied to the heater. The sample output voltage and the signals from thermocouples were continuously fed via an analog-to-digital converter to a personal computer for storage and processing. A difference between the readings of thermocouples at various temperatures of the sample was within 0–3 K.

Figure 1 shows a plot of the output voltage  $U$  generated in the sample versus temperature  $T$  (averaged over the readings of two thermocouples), which was measured in the regime of smooth gradual temperature increase. As can be seen, the output signal magnitude exhibits a jumplike increase at  $T_1 = 373$  K and a sharp drop at  $T_2 = 485$  K. Based on the existing model of the thermovoltaic effect, we believe that the voltage jumps in both cases are related to the screening of the Coulomb potential of excess samarium ions by the conduction electrons. At  $T = T_1$ , this results in a spontaneous collective activation of electrons from impurity (i.e. excess Sm) levels to the conduction band in



**Fig. 1.** Plot of the output voltage  $U$  generated in polycrystalline SmS due to the thermovoltaic effect at various temperatures  $T$ .

the region of the sample with a maximum local concentration of these levels  $N_{i(\max)}$ . As the temperature is increased, the activation proceeds in regions with smaller  $N_i$ . At  $T = T_2$ , the region of voltage generation goes out of a zone featuring the  $N_i$  gradient. This corresponds to  $N_i = N_{i0}$ , where  $N_{i0}$  is the concentration of donor impurity levels in the initial polycrystalline SmS.

According to [4], the electric field generated due to the thermovoltaic effect is as follows:

$$E = K \text{grad} N_i, \quad (2)$$

where  $K$  is the thermovoltaic coefficient. At  $T = T_2$ , the spontaneous collective activation of electrons takes place in the entire sample volume (rather than in the region where  $\text{grad} N_i \neq 0$ ) and the thermovoltaic effect ceases. This is a qualitative explanation of the experimental pattern of electric voltage variation in Fig. 1.

Using model notions based on the assumption of equality of the Bohr and Debye radii for defect (excess) samarium ions at the onset of generation [5], we may perform approximate calculations of various features of the thermovoltaic effect. The correctness of these notions was recently confirmed by calculations of the pressure of the semiconductor–metal phase transition in SmS in comparison to the experimental data [6].

An interesting feature of the thermovoltaic effect in SmS is the possibility of voltage generation in the sample at rather low temperatures (beginning from  $T = 300$  K). This feature is especially clearly pronounced in thin-film structures [7] and is also manifested in the

present case. As is known, the energy  $E_i$  for the impurity level activation in SmS-based materials (e.g., those with Sm excess in the homogeneity region) can vary up to  $E_i = 0$  [8]. In this context, we have studied the dependence of the generation onset temperature ( $T_1$ ) on  $E_i$ . It was also of interest to evaluate the range of  $T_2$  variation.

According to the published data, the donor level activation energy in stoichiometric SmS is  $E_i = 0.045 \pm 0.015$  eV. We have calculated the dependence of  $T_1$  on  $E_i$  in this interval using a method analogous to that in [4]. As the temperature increases, the thermo emf generation begins when the effective Bohr radius  $a_B$  becomes equal to the radius  $a_D$  of Debye screening of the electric potential of impurity atoms by the conduction electrons. These quantities are given by the following formulas:

$$a_B = \frac{\varepsilon_0 \hbar^2}{m^* e^2}, \quad a_D = \left[ \frac{4\sqrt{2} e^2 m^{*3/2} (k_0 T)^{1/2}}{\pi \varepsilon_0 \hbar^3} F_{1/2}(\mu) \right]^{-1/2}, \quad (3)$$

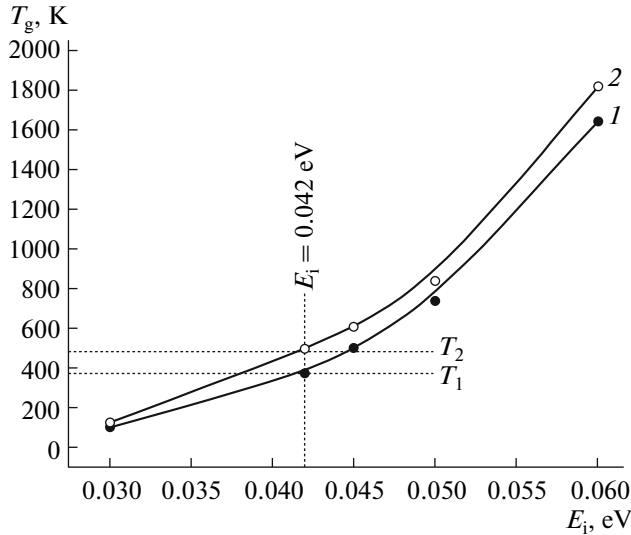
where  $\varepsilon_0 = 18$  is the static permittivity of SmS,

$$F_{1,2}(\mu) = \int_0^\infty (-\partial f_0 / \partial x) x^{1/2} dx,$$

$$f_0(x, \mu) = [1 + \exp(x - \mu)]^{-1}$$

is the Fermi integral, and  $\mu$  is the reduced chemical potential. Using the condition of  $a_B = a_D$  for  $m^* = m_0$  and  $E_i = 0.03$ – $0.06$  eV, we have numerically calculated the temperatures  $T_g$  at which the electrons from  $E_i$  levels are delocalized at an arbitrary degeneracy for various  $N_i$  values (Fig. 2).

Using the obtained family of  $T_g$  versus  $E_i$  curves (Fig. 2), it is possible to estimate the possible temperature interval of manifestation of the thermovoltaic effect in SmS and to evaluate the coefficient  $K$  in formula (2) for the sample studied. For this purpose, it is necessary to know the values of  $E_i$ ,  $N_{i(\max)}$ , and  $N_{i0}$ . The energy of activation of conduction electrons in the temperature interval of manifestation of the thermovoltaic effect in SmS was determined from the results of measurements of the temperature dependence of the electric resistance of the sample upon diffusion annealing. This temperature dependence was measured using the standard four-point-probe direct-current technique. As can be seen from the data presented in Fig. 3, the activation energy is  $E_i = 0.042$  eV. This value well agrees with the published  $E_i$  for stoichiometric SmS [5] without artificial  $\text{grad} N_i$ . This result appears to be quite reasonable only provided that the excess (overstoichiometric) samarium ions occupy in the crystal lattice the same positions as those of defect



**Fig. 2.** Dependences of the temperatures  $T_g$  of generation onset on the energy  $E_i$  of impurity electron levels, calculated using the proposed model for  $N_i = 10^{21}$  (1) and  $5 \times 10^{20} \text{ cm}^{-3}$ . Dashed lines correspond to the experimental values of  $T_1$ ,  $T_2$ , and  $E_i$ .

ions in the stoichiometric SmS, that is, occur at the boundaries of CSDs [9].

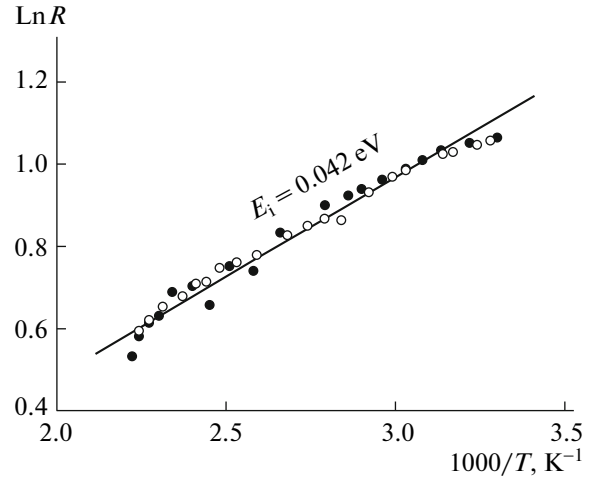
Then, the  $N_{i0}$  value can be estimated from the relationship between  $N_i$  and the CSD size, which was recently established in [10]. According to this, a CSD size of  $\sim 800 \text{ \AA}$  corresponds to  $N_i \sim 7 \times 10^{20} \text{ cm}^{-3}$ , which was assumed to be  $N_{i0}$ . On the other hand,  $N_{\text{max}}$  and  $N_{i0}$  can be estimated using the dependence presented in Fig. 2 and the experimental values of  $T_1$ ,  $T_2$ , and  $E_i$ . Considering  $N_i$  as the parameter and constructing model curves passing through these experimental points in the  $T_g$  versus  $E_i$  coordinates (see Fig. 2), we can determine the corresponding  $N_i$  values. In the case under consideration, these values are  $\sim 5 \times 10^{20}$  and  $10^{21} \text{ cm}^{-3}$ , which have to be assigned to  $N_{i0}$  and  $N_{i(\text{max})}$ . The data in Fig. 2 indicate that the generation in SmS is possible in a temperature range of  $T = 100\text{--}1800 \text{ K}$ .

Using the above data, it is possible to evaluate the gradient of concentration of excess samarium ions as follows:

$$\text{grad} N_i = \frac{N_{i(\text{max})} - N_{i0}}{x} = 10^{22} \text{ cm}^{-4}. \quad (4)$$

For the average value of the generated voltage ( $U = 17 \text{ mV}$ ), the electric field strength in the sample is

$$E = \frac{U}{x} = 0.34 \text{ V/cm}. \quad (5)$$



**Fig. 3.** Temperature dependence of the electric resistance of a polycrystalline SmS sample with graded concentration  $N_i$  of impurity levels, measured in the course of heating (black circles) and cooling (open circles).

Then, the thermovoltaic coefficient is estimated as

$$K = \frac{E}{\text{grad} N_i} = 3.4 \times 10^{-23} \text{ V cm}^3. \quad (6)$$

The degree of generality of the obtained results is yet unclear, since this is the first estimation of the thermovoltaic coefficient. The main difficulty consists in evaluating  $\text{grad} N_i$ . As was demonstrated [4], an effective increase in the thermovoltaic effect (i.e., the field  $E$ ) is provided only by doping SmS with excess (overstoichiometric) Sm ions to within 50.5 at. % (which corresponds to a composition of  $\text{Sm}_{1.02}\text{S}$ ). At the same time, modern measuring techniques only allow not less than 1 at. % of excess samarium in SmS to be detected.

**Acknowledgments.** This study was supported by the Russian Foundation for Basic Research (project no. 07-08-00289) and the SmS-Tenzo Company (St. Petersburg).

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*Translated by P. Pozdeev*